

TS-1030(US)
JDA:KNL

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PROCESS FOR THE PREPARATION OF STYRENEFIELD OF THE INVENTION

[0001] The present invention relates to a process for the preparation of styrene involving the gas phase dehydration of 1-phenylethanol at elevated temperature in the presence of a dehydration catalyst.

BACKGROUND OF THE INVENTION

[0002] A commonly known method for manufacturing styrene is the coproduction of propylene oxide and styrene starting from ethylbenzene. In general, this process involves the steps of (i) reacting ethylbenzene with oxygen or air to form ethylbenzene hydroperoxide, (ii) reacting the ethylbenzene hydroperoxide thus obtained with propene in the presence of an epoxidation catalyst to yield propylene oxide and 1-phenylethanol (also known as α -phenylethanol or methylphenylcarbinol), and (iii) converting the 1-phenylethanol into styrene by dehydration using a suitable dehydration catalyst.

[0003] The use of alumina catalysts in the dehydration of 1-phenylethanol per se is known in the art.

[0004] For instance, US 3,526,674 discloses the use of an alumina catalyst in the liquid phase dehydration of 1-phenylethanol into styrene, wherein said alumina catalyst suitably has a BET surface area of 40 to 250 m²/g and is used in finely divided form, i.e. in the form of particles having a particle size of 0.15 mm (100 mesh) or less.

[0005] US 3,658,928 discloses a process for the gas phase dehydration of 1-phenylethanol into styrene in the

presence of controlled amounts of added steam and in the presence of a catalyst, which suitably is a commercially available alumina catalyst like Harshaw Al-0104.

Harshaw Al-0104 catalyst has a pore volume of about

0.35 ml/g. A dehydration process using alumina (aluminium oxide: Al_2O_3) catalysts especially suitable for such

process has been disclosed in WO 99/58480. Use of these catalysts allows advantageous conversion of

1-phenylethanol into styrene without many of the

disadvantages of the use of prior art catalysts. However,

even use of these improved catalysts still leads to the

formation of heavy by-products, typically up to 5% of

oligomers and polymers of styrene. These heavy by-

products do not further convert and therefore decrease

the overall yield of desired styrene. Furthermore, these

high-molecular weight by-products tend to occupy the

pores of the catalyst, after which the catalyst can no

longer be used for converting 1-phenylethanol into

styrene. This necessitates a regeneration step of the

catalyst, which adds to the costs of the process.

[0006] It would be useful to find a catalyst for the gas phase dehydration of 1-phenylethanol into styrene,

wherein styrene is obtained at improved selectivity and

1-phenylethanol conversion can be maintained at a high

level for a longer time, thus requiring less frequent

catalyst regeneration.

SUMMARY OF THE INVENTION

[0007] The invention is directed to a process for the

preparation of styrene comprising the gas phase

dehydration of 1-phenylethanol at elevated temperature in

the presence of a dehydration catalyst, in which the

dehydration catalyst comprises shaped alumina catalyst

particles having a surface area (BET) of from 80 to 140 m²/g and a pore volume (Hg) of more than 0.65 ml/g.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

5 **[0008]** Within the context of the present application, the term "styrene" also embraces substituted styrenes, by which are meant styrenes containing one or more substituents bonded to the aromatic ring or to the vinyl group. Such substituents typically include alkyl groups, 10 such as methyl or ethyl groups. Similarly, the term "1-phenylethanol" also embraces substituted 1-phenyl-ethanols having the same substituents as the corresponding substituted styrenes.

15 **[0009]** It was found that an alumina dehydration catalyst wherein the catalyst has a BET surface area of from 80 m²/g to 140 m²/g and a pore volume (Hg) of more than 0.65 ml/g is suitable for the preparation of styrene by a gas phase dehydration of 1-phenylethanol at elevated temperature while the 1-phenylethanol dehydration was 20 maintained at a high level for a long time. Additionally, it was found that such process produced less heavy by-products than prior art catalysts.

25 **[0010]** The pore volume (Hg) of the catalyst for use in the present invention may be more than 0.65 ml/g. Preferably, the pore volume is at most 1.0 ml/g. More specifically, the catalyst preferably has a pore volume (Hg) of from 0.75 ml/g to 0.85 ml/g.

30 **[0011]** The BET surface area may be measured in any way known to be suitable to someone skilled in the art. The expression pore volume (Hg) stands for the pore volume as measured with mercury. Suitable methods for measuring the porosity with mercury are also well known to someone skilled in the art.

[0012] Shaped alumina catalysts with the properties required for use in this invention may be prepared by procedures known in the art, for example, by extrusion of alumina or alumina precursor pastes, followed by
5 calcination. Examples of alumina precursors are alumina hydrates such as aluminium oxide trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (also known as gibbsite or bayerite) and aluminium hydroxide, AlOOH (also known as boehmite or pseudo-boehmite). These alumina precursors are transformed to
10 alumina during the calcination process. Typically, in such a process, alumina powder or alumina precursor powder may be first optionally mixed with a binder powder. Suitable binder materials include inorganic
15 oxides such as oxides of silicon, magnesium, titanium, aluminium, zirconium, and silicon-aluminium. The weight ratio of binder to alumina powders may be from 0 (no binder present) up to 90:10. Typically, an extrudable mixture may be prepared from the solids (alumina powders and optionally binder) and water by mixing and kneading
20 the ingredients and passing this mixture into the extruder. Such extrudable mixture typically has a paste-like appearance. It is within the normal skills of those skilled in the art to optimize the mixing/kneading procedure to obtain an extrudable paste and to select the
25 most appropriate extrusion conditions. Besides the alumina, optional binder and water, the extrusion paste may also normally comprise extrusion aids to improve the extrusion process. Such extrusion aids may be those known in the art and include, for instance, peptizing agents
30 and flocculating agents. Peptizing agents facilitate a more dense packing of the particles in the extrusion mixture, while flocculating agents promote the inclusion of water. Suitable peptizing agents may be those known in

the art and include monovalent inorganic acids (e.g. hydrochloric acid and nitric acid) and organic acids such as aliphatic monocarboxylic acids, acyclic monocarboxylic acids, and fatty acids. Suitable flocculating agents may be those known in the art and include polyelectrolytes like those commercially available under the names NALCO® and SUPERFLOC®. Burnout materials may also be used to increase the porosity of the final extrudate. Examples of burnout materials are polyethylene oxide, methylcellulose, ethylcellulose, latex, starch, nut shells or flour, polyethylene or any of the polymeric microspheres or microwaxes.

[0013] A catalyst particularly suitable for use in this invention may be made from pseudo-boehmite (AlOOH). Such powder is commercially available from Criterion Catalyst Company.

[0014] The extrudable mixture or paste obtained as described above may then be subjected to an extrusion treatment. This extrusion treatment may be performed by conventional extrusion techniques known in the art. At the outlet of the extruder an orifice is present, which gives the extruded mixture the selected shape when leaving the extruder. When aiming to obtain spherically shaped extrudates, the wet extrudate is first spheronized in a suitable spheronizing device after having left the extruder before being subjected to calcination. The catalyst particles may have any shape, including spherical, cylindrical, trilobal, quadrilobal, star-shaped, ring-shaped, cross-shaped etc. The green extrudates obtained as described above are then optionally dried and subsequently subjected to a calcination step. A catalyst of the desired properties may be obtained by drying extrudates at temperatures of

from 100 °C to 140 °C for several hours and thereafter calcining at high temperature for several hours.

[0015] The dehydration of 1-phenylethanol into styrene according to the present invention may be carried out in the gas phase at elevated temperature. The term "elevated temperature" preferably is any temperature above 150 °C. The preferred dehydration conditions to be applied are those normally applied and include reaction temperatures of from 210 °C to 330 °C, more preferably of from 280 °C to 320 °C, and most preferably about 300 °C, and pressures in the range of from 0.1 bar to 10 bar, most preferably about 1 bara.

[0016] In the process according to the present invention the catalyst described hereinbefore has a reaction selectivity to styrene of at least 96% at a conversion of at least 99%, while selectivities of 97% or higher at conversions of 99% and higher have been achieved. In this connection, reaction selectivity is defined as the number of moles of styrene formed per mole of precursor compounds converted to products. Similarly, selectivities to other compounds such as heavy-ends are defined as the number of moles of precursor compounds to heavy-ends per mole of precursor compounds converted to products. Conversion is defined as the overall conversion level of 1-phenylethanol as determined under test conditions, i.e. the mole percentage of 1-phenylethanol converted relative to the total number of moles of 1-phenylethanol present in the feed. Furthermore, the selectivity of the catalyst towards heavy by-products like oligomers and ethers is very low: selectivity towards ethers typically is less than 0.8%, more suitably less than 0.3%, whereas selectivity towards oligomers typically is less than 3% and preferably 2% or less.

[0017] The invention will now be illustrated by the following examples without limiting the scope of the invention to these particular embodiments.

Example 1

5 [0018] A trilobe-shaped catalyst having the physical properties as indicated in Table I (Ex-1) was tested for dehydration performance in a microflow unit consisting of a 13 mm diameter plugflow reactor, 1-phenylethanol feed vaporization facilities and product vapor condensing
10 facilities. The 1-phenylethanol feedstock used was a sample of the process stream to the styrene reactor system of a commercial Propylene Oxide/Styrene Monomer plant. The feedstock contained 81.2% of 1-phenylethanol, 10.6% of methylphenylketone and 2% of water. The
15 remainder up to 100% consisted of impurities and (by)products of the preceding oxidation and epoxidation sections. The outlet stream of the micro flow unit was liquefied by condensation and the resulting two-phase liquid system was analyzed by means of gas chromatographic analysis.

20 [0019] The dehydration experiment was carried out at test conditions of 1.0 bara pressure and a temperature of 300 °C. The feed rate of 1-phenylethanol was maintained at 30 grams per hour and the reactor tube was loaded with
25 20 cm³ of catalyst. The reaction was continued for approximately 140 hours after which the experiment was stopped.

30 [0020] Activity (conversion) and reaction selectivity of the catalyst after 50 run hours were determined from the gas chromatographic analyses of reaction product samples. Activity after 120 hours was also measured. Data are reported in Table 1. Activity and selectivity have been defined above.

Example 2

[0021] The procedure as described in Example 1 was repeated, except that a different sample of feedstock containing 81.3% of 1-phenylethanol and 9.9% of methylphenylketone was used. Data are reported in Table 1 (Ex-2).

Comparison Example 1

[0022] The procedure as described in Example 1 was repeated, except that the trilobe-shaped catalyst had a BET surface area of 149 m². Physical properties are indicated in Table 1 (Comp-Ex-1). Only 1-phenylethanol conversion was monitored during the experiment, which was terminated after 98 hours, when 1-phenylethanol conversion was only 79%.

Comparison Example 2

[0023] The procedure as described in Example 1 was repeated, except that a star-shaped catalyst with physical properties within the ranges as described in the process according to WO 99/58480 was used. The reaction was continued for approximately 120 hours. Activity and selectivity data are given in Table 1 (Comp-Ex-2).

Comparison Example 3

[0024] The procedure as described in Example 1 was repeated, except that a trilobe-shaped catalyst with physical properties within the ranges as described in the process according to WO 99/58480 was used. A sample of feedstock containing 79.0% of 1-phenylethanol and 10.0% of methylphenylketone was used. Data are reported in Table 1 (Comp-Ex-3). The experiment was terminated after 113 hours, when 1-phenylethanol conversion was only 91%. Activity and selectivity data are given in Table 1 (Comp-Ex-3).

TABLE I Catalyst properties and performance

	Ex-1	Ex-2	Comp- Ex-1	Comp- Ex-2	Comp- Ex-3
Surface area (BET, m ² /g)	110	110	149	100	84
Pore Volume (Hg, ml/g)	0.77	0.77	0.84	0.57	0.44
Particle diameter (mm)	2.5	2.5	2.5	3.6	2.5
Conversion (%) after 50 h	99.9	99.9	98.0	99.7	99.9
Selectivity to styrene (%) after 50 h	96.5	96.5	(a)	95.9	95.0
Selectivity to heavy ends (ethers + oligomers) (%) after 50 h	3.0	3.0	(a)	3.5	4.3
Conversion(%) after 120 h	99.7	99.8	(b)	97.3	(c)

(a) Not determined

(b) Experiment stopped after 98 hours when conversion was 79%

(c) Experiment stopped after 113 hours when conversion was 91%